

**FIGURE 6**

Global NCOM SSH and surface currents in the Arabian Sea are compared with a MODIS composite produced by the Ocean Optics section at NRL (Ocean Color at <http://www7300.nrlssc.navy.mil/products.html>). Eddies located in the global NCOM analysis agree with observed features delineated by gradients in diffuse attenuation coefficient.

thank Ms. J. Dastugue for her assistance in developing the Global NCOM web site at [www.ocean.nrlssc.navy.mil/global\\_ncom](http://www.ocean.nrlssc.navy.mil/global_ncom). This work is made possible through the support of Space and Naval Warfare Systems Command PMW155 and computational resources provided by the Department of Defense High Performance Computing Modernization Program.

[Sponsored by SPAWAR]

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## THE INFLUENCE OF MICROBIAL Fe(III) REDUCTION ON CLAYEY SEDIMENT FLOCCULATION

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**Introduction:** Understanding the role of flocculation of suspended sediments carried by rivers is important to industries and naval undersea operations. This "fluid mud" can be responsible for the variability of littoral sediment properties such as turbidity, shear strength, and compressibility. Many theoretical and laboratory studies have dealt with the physical chemistry and fluid dynamics of interactions among sedi-

mentary particles.<sup>1</sup> Nevertheless, previous studies have given little consideration to the environmental variables that are important in the actual sedimentary environment such as the variability of particle compositions (i.e., bacteria, particulate organic matter, and clay mineralogy) and the temporal and spatial dynamics of redox chemistry controlled by the microbial diagenesis. Furthermore, few direct observations of suspended particles in fluid mud were reported, which may be due to the difficulties of sampling or handling the materials. In this study, we aim to quantify the role of microbial diagenesis in controlling particle flocculation.

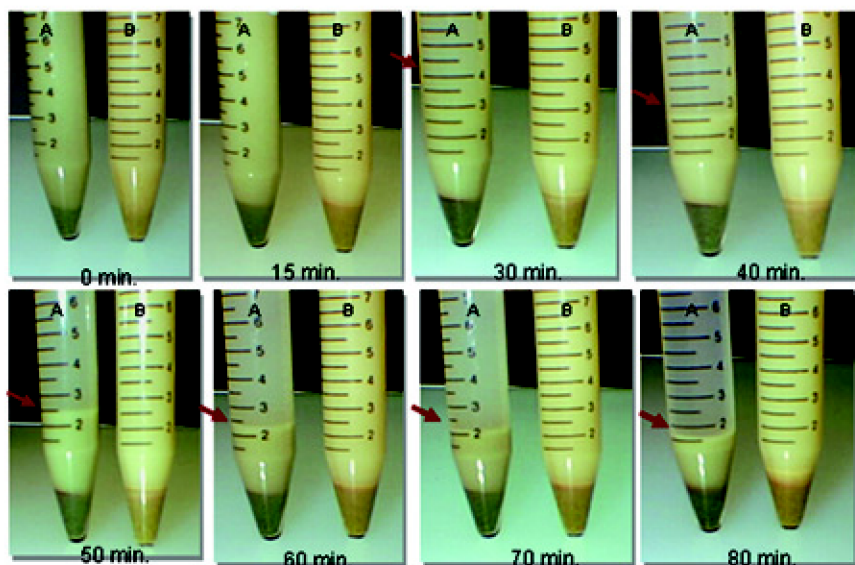
**Material and Methods:** Nontronite from the Uley graphite mine, South Australia (Clay Mineral Society standard, NAu-1) was used in this study. Nontronite is an iron-rich smectite widely distributed in marine and terrestrial environments. Powdered nontronite (< 0.2 mm) and iron-reducing bacterium, *S. oneidensis*, were mixed in a tube, and then incubated anaerobically for 48 hours. Similarly, a control lacking cells was prepared and incubated. Reduced and nonreduced (control) nontronite were then suspended in separate settling columns placed in an anaerobic chamber. The size distribution of suspended aggregate particles and their settling velocity was measured using a Micromeritics Sedigraph and calculated based on Stokes' Law. A JEOL JEM-3010 transmission electron microscope (TEM) operating at 300 keV was used to characterize changes in the floc architecture, in particular the changes in structure of nontronite particles that were induced by microbial reduction of Fe(III) in nontronite. Reference 2 provides details of sample preparation and experimental methods.

**Results:** Figure 7 shows the reduced nontronite (with cells) in settling tube A and the nonreduced nontronite (without cells) in settling tube B. The substantial color change of clay that resulted from reduction of Fe(III) is apparent in tube A compared to tube B, which displays the original color of the clay. The reduced nontronite suspension began to flocculate in 30 minutes, as indicated by the arrow, and was almost completely settled in 80 minutes (tube A). In contrast, the controlled nontronite suspension remained dispersed in the water column, even after 80 minutes (tube B). Nontronite aggregate size distributions were measured using a Micromeritics Sedigraph in various durations of incubation time (0 – 48 hr) compared to controlled nontronite, as shown in Fig. 8. Depending on a given condition, the reduced nontronite suspen-

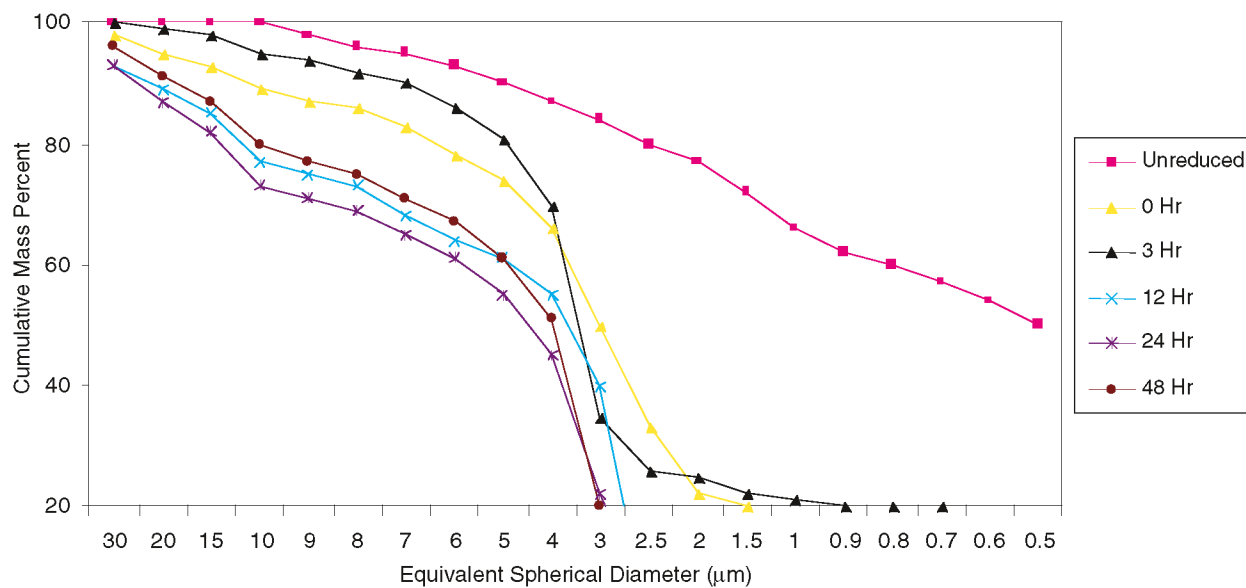
sions show variations of aggregate sizes ranging from 2.5 to 4  $\mu\text{m}$  in equivalent spherical diameter at 50 cumulative mass percent, which is about 5 to 8 times larger than controlled suspensions (0.5  $\mu\text{m}$ ). The calculated mean settling velocity of reduced nontronite suspensions is  $6.9 \times 10^{-4}$  cm/s based on 25 degrees in temperature, average grain density = 2.5 g/cc, and average grain size = 3.2  $\mu\text{m}$ , while  $2.1 \times 10^{-5}$  cm/s averaged settling velocity is calculated for nonreduced nontronite suspensions with 0.5- $\mu\text{m}$  average grain size. The aggregate size distributions of 0- and 3-hour incubation experiments are similar, and 12-, 24-, and 48-hour incubation experiments are similar. Previous studies have shown that there is no structural Fe(III) reduction at 0 hour, and less than 10% of total structural Fe(III) is reduced to Fe(II) within the first 3 hours of incubation.<sup>3</sup> Consequently, the formation of flocs in these samples is considered to be controlled by microbial biopolymers rather than by the change in particle redox chemistry. However, small aggregates (less than 2.5  $\mu\text{m}$ ) are found only in 0 to 3 hour samples, not in 12 to 48 hour samples, suggesting the role of further microbial reduction of clay layers and further production of biopolymers in coagulation of small aggregates into larger macro-flocs.

The TEM-imaged floc architectures of the control and reduced nontronite suspensions are illustrated in Fig. 9(a) and 9(b), respectively. Typically, hexagonal-shaped single nontronite particles are well-dispersed, and large pore areas are dominant features of nonreduced nontronite (Fig. 9(a)). In comparison, reduced nontronite occurs in clusters containing *S. oneidensis* (S) and biopolymers with few if any pore areas observed (Fig. 9(b)). The structural changes in nontronite upon Fe(III) reduction are shown in Fig. 9(c) and 9(d). The mean basal layer spacing decreases from 1.5 to 1.2 nm, and the diffuse ring patterns in the selected area diffraction (SAED) patterns gain discrete Bragg reflections upon Fe(III) reduction. The structural changes are mainly caused by the increase in net negative charge on reduced nontronite; therefore, coagulation of the clay particles is accelerated by cations such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ .

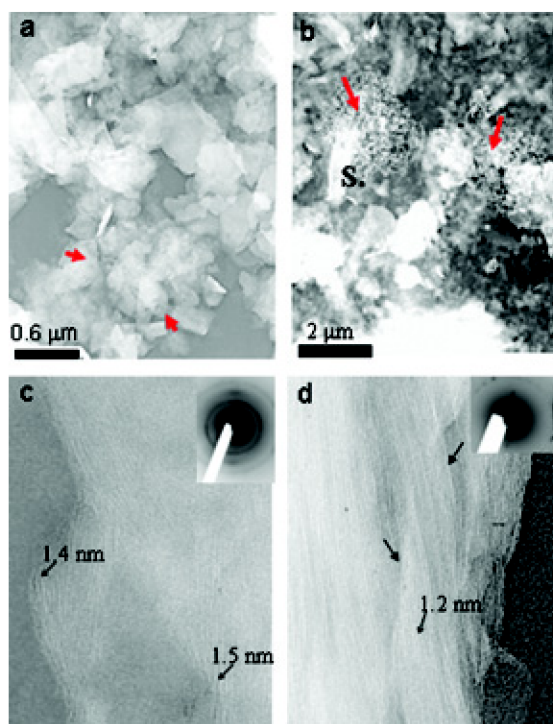
**Conclusions:** Microbial Fe(III) reduction promotes the flocculation properties of clay particles: (1) biopolymers play an important role of forming micro-flocs of dispersed nonreduced clay particles (<2.5  $\mu\text{m}$ ); (2) upon microbial Fe(III) reduction, both surface charges increase and further production of biopolymers promotes the coagulation of clay aggregates forming macro-flocs (>2.5  $\mu\text{m}$ ).



**FIGURE 7**  
Settling behavior of microbially Fe(III) reduced nontronite suspensions (tube A) and non-reduced (control) nontronite suspensions (tube B).



**FIGURE 8**  
Aggregate size distribution of nonreduced (control) nontronite and microbially Fe(III) reduced nontronite suspensions (over 48 hours).



**FIGURE 9**

Conventional transmission electron microscopy (TEM) micrographs of floc architectures of (a) nonreduced (control) nontronite suspensions and (b) microbially Fe(III) reduced nontronite suspensions inoculated with *S. oneidensis* (S). Environmental cell (EC)-(TEM) micrographs with selected area electron diffraction (SAED) patterns showing; (c) nonreduced (control) nontronite (lattice fringe spacing  $\approx 1.4 - 1.5$  nm) and (d) reduced nontronite (lattice fringe spacing  $\approx 1.2$  nm).

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## DISSOCIATION OF SUB-SEAFLOOR GAS HYDRATES AND SEAFLOOR STABILITY: WHAT THERMOBARIC MODELS SHOW

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**Introduction:** Gas hydrates, which are stable at the high pressures of seafloor more than a few hundred meters deep, are crystalline solids with a cage-like (clathrate) structure of water molecules enclosing larger host molecules, most commonly methane. The material is present between sediment grains or in larger veins and nodules under most continental

margins, with enormous aggregate volumes. Ongoing research, some at NRL, is motivated by the potential use of hydrates as a fuel source, the possible release of greenhouse gas by hydrate dissociation, and the influence of such dissociation on seafloor sediment stability, which forms the basis for our study.

The association of undersea landslides with geophysical evidence for hydrates below the U.S. East Coast continental slope led G. Carpenter to hypothesize in 1981 that low sea levels of the last Ice Age (ca. 18,000 years ago, abbreviated 18ka (millenia ago)) may have caused hydrate to dissociate at depth, reducing sediment shear strength and facilitating failure. Other researchers elaborated on this idea—suggesting that the methane liberated by slides could have warmed the atmosphere, forming a "shut-off valve" for ice ages. While these ideas have gained wide acceptance, Norwegian scientists found the three major slides they studied along their margin (Fig. 10) to have happened when they should not—during the rapidly rising sealevels of post-glacial times. The largest (Storegga, 5,500 cubic kilometers!) and best known slide—and one that NRL and Norwegian collaborators have studied, including 1999 dives by USN nuclear submarine NR-1—occurred 8,150 years ago (8.15ka), generating a major tsunami. Intrigued by this contradiction but still suspicious that hydrate dissociation helped cause the failures, we began modeling the evolution of the gas hydrate stability zone at Storegga and other margins.